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ACID PRESSURE LEACHING OF A SULPHIDIC URANIUM ORE WITH EMPHASIS ON THE PROBLEM OF RADIUM EXTRACTION

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ACID PRESSURE LEACHING OF A SULPHIDIC URANIUM ORE WITH EMPHASIS ON THE PROBLEM OF RADIUM EXTRACTION

by

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ABSTRACT

A pressure loading study of a pyrite-containing uranium ore from Elliot Lake, Ontario was conducted to affect simultaneous extraction of uranium and radium thereby producing tailings with reduced environmental impact.

This investigation was carried out in two parts. In Part I, pressure leaching with only oxygen gas was studied. By varying the experimental parameters: temperature, oxygen pressure, retention time and pulp density, optimum oxidation conditions were established for the production of sufficient H_2SO_4 and Fe^{3+} necessary for uranium dissolution with minimal excess of sulphate ions. Thus high uranium extraction (>93%) and increased radium mobility (30% extraction) were obtained at 125°C, 345 kPa U_2, 6 h and 50% solids.

In Part II, enhancement of radium extraction was sought by various salt chloride additions to the pressure leach slurry with mixtures of $CoCl_2$/HCL found to give the best performance. The final radium-226 level in leach residue was found to be controlled ultimately by the applied ratio of $CaCl_2$ addition to solids used.

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Thus a pulp density of 25% solids with addition of 2.0 M $CaCl_2$/ 0.1 M HCl at 125°C and 345 kPa O_2 yielded 96% uranium and 91% radium (36 pCi/g residual Ra^{220}) extractions respectively. A two-stage leach scheme was also investigated involving atmospheric leaching with $CuCl_2$/HCl at 70°C as a second stage for the treatment of the pressure leach residues. Improvements in overall radium extraction were again realized yielding ultimately tailings almost free of radionuclides.

Thorium, rare earths and other significant ore components were also monitored throughout this test work.

LIXIVIATION SOUS PRESSION DE L'ACIDE D'UN MINERAI D'URANIUM SULFURÉ EN PORTANT UN INTÉRÊT PARTICULIER AU PROBLÈME RELIÉ À L'ÉXTRACTION D'URANIUM

par

P. Demopoulos*

RÉSUMÉ

On a effectué une étude sur le chargement sous pression d'un minerai de pyrite contenant de l'uranium, extrait à Elliot Lake en Ontario, pour en vérifier les effets sur l'extraction simultanée de l'uranium et du radium pour produire des résidus dont l'effet sur l'environnement est diminué.

Cette enquête comprend deux volets. Le premier a porté sur l'étude de la lixiviation sous pression en utilisant seulement de l'oxygène. En faisant varier les paramètres expérimentaux, soient la température, la pression de l'oxygène, le temps de rétention et la densité de la pulpe, on a pu établir les conditions optimales d'oxydation pour produire suffisamment de H_2SO_4 et de Fe^{3+} pour dissoudre l'uranium et obtenir un excès minimal d'ions sulfate. On a pu obtenir de cette façon, un pourcentage élevé d'extraction d'uranium (>93%) et l'augmentation de la mobilité du radium (extraction à 30%), à 125°C, 345 kPa U_2, 6 heures et 50% de solides.

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Dans le deuxième volet, on a cherché à augmenter l'extraction d'uranium par diverses additions de chlorure de sel à la boue lixiviée sous pression. On a obtenu les meilleurs résultats avec des mélanges de $CoCl_2$ et HCl. On a trouvé que le niveau final de radium-226 dans le résidue de lixiviation est contrôlé finalement pas le rapport appliqué de l'addition de $CaCl_2$ aux solides utilisés.

INTRODUCTION

Present methods of extracting uranium from its ores involve leaching with sulphuric acid or alkaline (carbonate) solutions, depending upon the ore mineralogy (1). In either extractive process only uranium is recovered from the ore, while the rest of the radionuclides including radium-226 reports to the tailings (2). Weathering and/or bacterially promoted oxidation of sulphides contained in these tailings (i.e., Elliot Lake, Ontario) result in environmentally unacceptable high levels of radium releases into neighbouring streams (3).

The prevention of these radium releases during the operating life of the mine-mill complex is effected in most cases by adding limestone to the tailings slurries to counter bacterial acid generation and by adding barium chloride solution to liquid effluents to coprecipitate radium as radium barium sulphate. However, the long term containment of these radionuclides remains a serious and as yet unsolved problem. Many investigations aimed at alleviating the adverse environmental impact of these uranium mill tailings have been carried out. The principal objective of these investigations was to remove radium from the tailings (4,5).

In addition to the problem of tailings stability, sulphuric acid leaching, as it is practiced today in Elliot Lake, Ontario, is associated with slow kinetics (>40 h leaching time) and losses of potentially useful byproducts such as thorium and rare earths. Thus an alternative leaching system should be developed to meet the requirements of an environmentally acceptable process with simultaneous maximization of uranium recovery, possible recovery of byproducts and a simplified flowsheet. A simple ore treatment process that would solubilize all or most of the radium together with uranium and possibly thorium and rare earths is the desirable one (6,7).

Both nitric and hydrochloric acid systems have been tested as alternatives to sulphuric acid with the latter found to be the most promising one (8).

In addition to ambient pressure leaching systems, leaching under pressure (at temperatures above the boiling point of water with oxygen over-pressures) could be an alternative system. In fact this approach has been proposed for uranium extraction from sulphidic type ores found in Canada (9), Australia (10) and South Africa (11) as long ago as the mid 1950's.

Further studies conducted on various ores from the Elliot Lake area at the Mines Branch (now CANMET) (12,13), confirmed the effectiveness of the oxidation pressure leaching process. Gow and Ritcey (14) and Dasher (15) have critically evaluated its applicability in the uranium industry and have indicated equivalent or substantially reduced capital and operating costs in comparison with the conventional practice. Among the advantages of pressure leaching are: low or no H_2SO_4 addition; fast kinetics and high uranium recoveries. However all previous works reported in the literature are concerned only with uranium recovery without any attention being given to the radium problem outlined above and the recovery of byproducts.

More recently the interest in pressure leaching has been impressively revived because of the treatment of the refractory sulphidic uranium ores of South Africa and the newly discovered complex high-grade ores of Northern Saskatchewan. In South Africa the successful operation of a 'prototype' pressure leach pilot plant (16) led to the decision by Anglo American Corporation to proceed with the installation of two very large pressure leaching plants (17) for which Sherritt Gordon Mines provided the process engineering design (18). The first pressure leaching plant with a uranium ore capacity of 600 000 t/a has already been constructed while construction of the second one of nearly 3 000 000 t/a ore capacity has yet to commence. Justification for these two large pressure leach installations was made on the grounds of lower operating costs and significantly higher recoveries (17). Another recent interesting development related to the pressure leaching of South African uranium ores was the installation of a third plant of 500 000 t/a ore capacity (17) where the VAW tube digester available from Lurgi (19) found its first application outside the alumina industry.

The very high-grade uranium/nickel/arsenic ores of Northern Saskatchewan pressure leaching proved again the preferred treatment process. Extensive test work showed that this method gave consistently high yields of uranium into the leach solution even when there was considerable variation of other major elements (e.g., arsenic and nickel). Thus the Key Lake uranium process was developed based on a mild pressure leaching in sulphuric acid in the second stage of a two-stage system (20,21). The plant for the treatment of Key Lake ores is presently being constructed and is expected to come into operation soon (1983/84). Leaching in autoclaves using sulphuric acid and oxygen is also considered for the treatment of the Midwest uranium deposit which is remarkably similar to the Key Lake deposits (22,23).

In view therefore of the impressively increasing role played by acid pressure leaching in the uranium extraction industry both in Canada and elsewhere and the urgent need for environmentally acceptable processes producing radium-free tailings, this work was initiated to evaluate the possibility of tackling simultaneously the problems of high uranium and radium dissolution during pressure leaching (no other work has been conducted previously in that direction). A pyrite containing uranium ore from Elliot Lake, Ontario was used for the work reported here, while further studies are currently directed into the complex and high-grade uranium ores of Northern Saskatchewan.

THEORETICAL CONSIDERATIONS

URANIUM EXTRACTION

Effective leaching of uranium from most of its ores is accomplished by the combined action of sulphuric acid and ferric iron (24,25,26). The former is required for the direct non-oxidative dissolution of hexavalent uranium (Eq 1) and the latter for the oxidative dissolution of tetravalent uranium (Eq 2).

$$UO_3 + 2H^+ \rightarrow UO_2^{2+} + H_2O \qquad \text{Eq 1}$$

$$UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+} \qquad \text{Eq 2}$$

Therefore, a high ferric ion concentration or more precisely a high Fe^{3+}/Fe^{2+} ratio (27) (which determines the redox potential) is of vital importance in ensuring fast kinetics and high overall extraction levels. Iron is always found in sufficient quantities in the ore to satisfy the leaching reaction requirements.

PYRITE OXIDATION

Regeneration of ferric iron in conventional atmospheric leach practice is achieved by adding various strong chemical oxidizing reagents and most commonly $NaClO_3$ or MnO_2, while in pressure leaching, oxygen gas is employed instead (Eq 3).

$$2Fe^{2+} + 2H^+ + {}^1/_2O_2 \rightarrow 2Fe^{3+} + H_2O \qquad \text{Eq 3}$$

The oxidation of ferrous iron in a sulphuric acid medium by oxygen has been studied extensively (28,29,30) and the reaction rate has been found to be of second order with respect to $[Fe^{2+}]^2$ and of first order with respect to PO_2. Also, it has been found that an increase in sulphuric acid concentration results in the decrease of reaction rate while if the same reaction is conducted in hydrochloric acid solution, an increase in acid concentration results in an increase in the oxidation rate (30). The presence of cupric ions has also been found to catalyze significantly the above reaction (Eq 3) (28,29).

While in conventional atmospheric leaching sulphuric acid is added to satisfy the acid requirements of the process, pressure leaching of sulphidic uranium ores makes little or no use of external sulphuric acid. The reason is the in situ generation of sulphuric acid during pressure leaching of the uranium ore according to the following reaction.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad \text{Eq 4}$$

This exothermic reaction (Eq 4) represents the oxidation of pyrite to produce the soluble iron and sulphuric acid necessary for the dissolution of uranium. The extent to which reaction (Eq 4) would progress defines in a large measure the amount of oxygen consumed during pressure leaching and hence the economics of the process since oxygen is the most costly reagent used. The aqueous oxidation of pyrite (under conditions applicable to pressure leachng of uranium ore) has been investigated by Warren (31) and McKay and Halpern (28) in two separate but complementary studies with the former conducted at 130 to 210°C and the latter at 100 to 130°C. Experimental variables which accelerate pyrite oxidation are fine grind (28), increased oxygen pressure (PO_2) (28,31), reaction temperature (28,31) and small oxygen bubble diameter (32). Again according to the cited literature information, temperatures above 130°C favour oxidation of sulphide sulphur to sulphate form only, while at lower temperatures (100-130°C) elemental sulphur in considerable measure (nearly 50% of the oxidized sulphur) is also produced. In addition to lower temperatures, production of elemental sulphur is also favoured by high acidities and short retention times (28). Thus reactions (Eq 5) and (Eq 6) might also take place during pressure leaching of sulphidic uranium ores (28):

$$FeS_2 + 2O_2 \rightarrow FeSO_4 + S^\circ \qquad \text{Eq 5}$$

$$2S^\circ + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \text{Eq 6}$$

Another reaction which should be considered in a pressure leaching system is the hydrolysis of the ferric ion:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad \text{Eq 7}$$

At 25°C, this reaction is avoided by simply keeping the pH of the solution less than 2: however, at higher temperatures hydrolysis of Fe^{3+} in fact takes place at even lower pH and at faster rates. Above 130°C ferric iron tends to precipitate fairly rapidly even from solutions of pH as low as 1 forming simple or/and complex basic oxides (29,33). This hydrolytic reaction is undesirable since it not only removes ferric iron from solution which is required for the dissolution of uranium (Eq 2) but also makes filtration process very difficult (16).

RADIUM EXTRACTION

Experimental evidence from several investigations reported in literature (2) and theoretical considerations (radium as a daughter of the radioactive decay of uranium is incorporated to the mineral structure of the latter) lead to the conclusion that radium is expected to be disolved along with uranium during leaching. However, due to the very low solubilities of its sulphate salt H_2SO_4 (acid leaching) and its carbonate salt (alkaline leaching) precipitation occurs resulting in most of radium reporting in the leach residue. Coprecipitation, adsorption or ion exchange phenomena further contribute to removal of radium from leach solutions.

Effective control of the sulphate ion concentration during leaching is therefore considered mandatory if high radium extraction is sought. From a number of studies on radium extraction from uranium ores or tailings reported earlier [these are well summarized by Itzkovitch and Ritcey (2)] or more recently (8,34,35,36,37,38) it can be concluded that factors such as low pH (controlled by HCl), short retention times, low pulp density and the presence of competing complexing anions would further increase radium extraction.

OUTLINE OF RESEARCH APPROACH

Through a combination of experimental variables (temperature, oxygen pressure, pulp density, retention time, catalysts) optimum oxidation conditions were established for the production of sufficient H_2SO_4 and Fe^{3+} necessary for high uranium extraction with simultaneously minimal excess of sulphate ions thereby allowing higher radium mobility. Subsequently the addition of various salt chlorides was investigated with the objective of maximizing radium extraction. Extraction levels of thorium and rare earths were also monitored throughout this work.

EXPERIMENTAL

ORE

The uranium ore was obtained from the Elliot Lake area (Quirke mine, Rio Algom Ltd) and consisted of a pyritic quartz pebble conglomerate (39,40). Typical chemical analysis of the ore used in this work is shown in Table 1. The ore samples were ground to 63% minus 200 mesh. Brannerite is the major uranium bearing mineral, but uraninite and monazite are also present in the ore (39). Most of the thorium and rare earth contents are associated with monazite which is a very refractory ore. Pyrite is the main sulphide mineral. According to the chemical analysis shown in Table 1, the iron content is much higher than the amount expected if it is assumed that all sulphide sulphur of the ore is associated with pyrite only. Most likely therefore, some pyrrhotite is also present (39). Iron oxides as well as iron introduced during grinding might also be the reason for the higher iron content.

APPARATUS AND PROCEDURE

Leaching tests were conducted in a 2-l titanium autoclave supplied by Parr Instrument Company, Moline, Illinois. An aqueous slurry of the feed was heated to the required temperature under slight nitrogen overpressure (i.e., air was excluded). Chemical additions (if applicable) were introduced at reaction temperature through a specially adapted pressurized chamber. Oxygen was also admitted at reaction temperature (time zero) under the slurry surface to ensure good gas dispersion. The oxygen pressure reported here is the difference between the total pressure measured after oxygen introduction and that before. The autoclave was connected throughout the course of a

leaching test to the oxygen cylinder thereby allowing continuous supply of oxygen at the pre-set pressure level. Agitation was provided by two 6-bladed axial) turbine impellers at a constant rate of 450 rpm. Temperature control was maintained at 2°C throughout the test except at the initial stage of the reaction when the introduction of the cool mass of oxygen gas caused a temperature drop of 5-10°C. The temperature drop was quickly compensated by the heat released from the exothermic oxidation of pyrite which resulted in equivalent temperature excess over the set point. In most of the tests stable temperature control was established after the first half hour since oxygen introduction.

The progress of the leaching reactions was monitored by withdrawing slurry samples at appropriate intervals through a 1/4" sampling port equipped with a ball valve. The samples were filtered immediately after collection and the residues were washed repeatedly: twice with acidified distilled water (0.25 vol% H_2SO_4 or 1.0 vol% HCl the latter used for those tests where chloride additives were involved) and finally once with distilled water at room temperature. All the washings were conducted with approximately the same solid to liquid ratio like the one used for each test. Repulping of some residues with more acidified water showed no significant change in uranium and radium contents. Pregnant, combined wash solutions and dried (at 90°C for at least 24 h) residues were sent for appropriate analysis.

Leaching efficiencies were determined based on the dried solids assayes. Correction factors were applied to account for the solids weight losses during leaching (3% after 6 h leach). Solution concentrations for uranium were slightly higher than those expected from mass balance calculations due to evaporation losses during sampling as well as due to some solution retained in residue after filtration. In contrast solution concentrations for radium and sulphate ion were systematically lower, the former believed to be due to precipitation of $RaSO_4$ by the time analysis was conducted and the latter due to gross interferences of the complex solution composition with the applied barium sulphate method (41). A few extra words concerning radium analytical results are considered appropriate. Some liquid samples after radium analysis had been conducted were acidified with HCl and were sent again for analysis. Readings up to ten times higher than those in the first place were obtained. With no immediate washing of residues after filtration (while they are still hot) might also result in low radium extraction values. The pH and EMF (in reference to a saturated calomel electrode) of the pregnant solutions were also monitored.

RESULTS AND DISCUSSION

PART I - PRESSURE LEACHING WITHOUT REAGENTS

Uranium, Radium and Sulphur Extraction

In this series of experiments apart from oxygen gas no other reagents were added. The experimental variables investigated were: retention time (1 to 6 hours), temperature (125 to 175°C), partial oxygen pressure [103 to 517 kPa (15 to 75 psi)] and pulp density (40 to 60% solids). Overall extraction data for uranium, radium and sulphur obtained after 6 h leaches under various conditions are summarized in Table 2. Sulphur extraction results are an indirect measure of the sulphate sulphur reported in solution which to a large extent controls radium extraction. Leaching rates for uranium and radium are presented in the form of per cent extraction versus retention time.

The effect of temperature on uranium and radium extraction is illustrated in Fig. 1. For these tests a pulp density of 60% solids and a partial oxygen pressure of 103 kPa (15 psi) were employed. For all tests described in Fig. 1 as well as those described later, uranium extraction was higher than 80% after 1 h leach. Subsequent uranium extraction increased at a much slower rate. No measurable improvement in uranium extraction was observed by increasing temperature from 150 up to 175°C. Maximum uranium extraction was 94% after 6 hours leaching at 150°C (or 175°C).

Radium extraction was significantly lower than that of uranium with the best extraction obtained (35%) at 150°C and 6 h retention time. Leaching at 175°C resulted in minimal radium extraction this being apparently due to high sulphate production at this temperature (see Table 2). Radium extraction at 125°C was lower than that obtained at 150°C despite a lower sulphur extraction (see Table 2). In addition to difficulties associated with radium analysis, the combined effect of higher temperature (discussed later) and lower pH (see Fig. 5), might also be contributing to this "anomaly". Nevertheless, the results of Fig. 1 clearly suggest that temperatures above 150°C should be avoided since radium extraction is severely minimized without at the same time obtaining measurable gains in uranium recovery.

The effect of partial oxygen pressure on uranium and radium extraction is shown in Fig. 2. Standard conditions for these tests were 125°C and 60% solids. An improvement on uranium extraction was realized by increasing oxygen pressure from 103 kPa (15 psi) to 345 kPa (50 psi) but further increase

of pressure to 517 kPa (75 psi) did not have any significant effect. Radium extraction was not significantly affected by the variation of oxygen pressure at 125°C. Apart from some minor fluctuations of radium extraction with time believed to be due to difficulties associated with sample preparation and analysis, radium extraction was between 20 to 30% after 6 h leach. Therefore partial oxygen pressure of 345 kPa is considered optimum for tests conducted at 125°C. For tests conducted at 150°C, a partial oxygen pressure of 103 kPa O_2 would be the optimum since 345 kPa O_2 was found to result in lower radium extraction due to increased sulphur extraction (see Table 2).

In Fig. 3 percent extraction of uranium and radium versus retention time are shown for three different pulp densities. Standard experimental conditions for these tests were 125°C and 345 kPa O_2. Final uranium extraction (6 h leach time) dropped slightly from 94.5 to 93.0% for the tests conducted at lower than 60% solids pulp density (i.e., 50 and 40% solids). At the same time final radium extraction levels (6 h leach time) were slightly improved for the low pulp density tests. These results suggest that gains may be expected with lower pulp densities relating to radium extraction but some small penalty in uranium extraction would have to be paid in this case.

Solution Chemistry

In the previous section on Theoretical Considerations discussion showed that sulphate ion concentration, acid concentration (or equivalently pH) and Fe^{3+}/Fe^{2+} ratio (i.e., EMF) are the major parameters controlling uranium and radium extraction. Thus these three solution components were monitored throughout this testwork and the obtained results for the tests conducted at 125 and 150°C (which were identified as the most suitable in achieving simultaneously high uranium extraction and high radium mobility) are presented in Fig. 4, 5 and 6. Plotted sulphate concentrations of Fig. 4 are not actual measured values but they were calculated from sulphur extraction data based on residue analyses assuming that all sulphur reported in solution is in sulphate form. This approach was adopted to overcome problems associated with direct analysis of solution sulphate concentrations discussed in the experimental section. The results of Fig. 4 and Table 2 suggest that radium up to 30% is extracted even at sulphate concentrations as high as 40g/L. This concentration is comparable to that encountered in conventional atmospheric leach solutions where radium extraction is minimal. It is also higher than the

theoretically calculated value from the solubility product of $RaSO_4$ (42a). The two leaches, pressure vs atmospheric, differ in temperature, pressure and retention time (70°C and 48 h respectively for atmospheric leach). Thus the higher radium mobility observed when pressure leach is employed is most likely due to these factors. No directly measured data on $RaSO_4$ solubility are available in literature, however, published data (43) concerning $BaSO_4$ [which is considered exhibiting similar behaviour with $RaSO_4$ (42a)] in fact suggest higher solubility at higher temperatures (44). Nevertheless, it seems to us that kinetic rather than equilibrium reasons (short retention time) are mostly responsible for the observed higher radium solubility (slow precipitation of $RaSO_4$).

In Fig. 5 the variation of pH with leaching time is illustrated. These results in combination with those reported in Table 2 suggest that a terminal pH of less than 1.25 is necessary for obtaining at least 94% uranium extraction. In Fig. 6 the corresponding Fe^{3+}/Fe^{2+} ratios as well as the measured redox potentials (relative to a saturated calomel electrode) for the same group of tests are plotted. The beneficial effects of temperature, oxygen pressure and retention time are indicated. From a practical point of view equivalent leaching results are obtained by either operating at 125°C and 345 kPa O_2 or at 150°C and 103 kPa O_2. The EMF measurements show that during pressure leaching redox potential is kept relatively high and even increases with time level, a condition identified previously as important for improved leaching efficiencies (45).

The effect of pulp density on solution chemistry and resulting leaching efficiencies for uranium and radium is shown in Table 3. The somewhat diluted leach solutions resulting when lower solids concentrations are used explains the observed changes in uranium (decrease) and radium (increase) extraction. These findings are in agreement with McKay and Halpern's work (28) showing that the oxidation rate of pyrite is proportional to the mineral surface area.

McKay and Halpern (28) had also shown that ferrous to ferric oxidation can be catalysed by copper sulphate. Thus to improve the somewhat low Fe^{3+}/Fe^{2+} ratio of the low pulp density experiments a test was conducted in presence of 0.1 M $CuSO_4$. Ferric to ferrous ratio (and thereby the solution redox potential) was in fact significantly increased as the results of Table 4 show, but no overall uranium extraction gains were observed in this particular

case. However, this approach remains an effective means in catalysing $Fe^{2+} \rightarrow Fe^{3+}$ oxidation with molecular oxygen whenever this is considered desirable.

Distribution of Sulphur and Iron

McKay and Halpern (28) are the only investigators who have reported significant elemental sulphur formation from pyrite oxidation during pressure leaching. It was of interest therefore to examine if in fact elemental sulphur is formed under the conditions applied in the present work. Selected residue samples were analysed and some typical results indicating the distribution of various sulphur species are summarized in Table 5. Although the presented results by no means are considered complete, however, a trend clearly is seen of significant elemental sulphur formation especially at lower temperatures - a finding confirming previous results (28).

Thus further studies, which will elucidate the mechanism of elemental sulphur production under practical pressure leaching conditions and identify means for maximizing sulphur extraction in elemental form while sulphate formation is kept low, would be of great importance to uranium hydrometallurgists. By extracting most of sulphur in this way, high radium extraction (low sulphate production) and simultaneous pyrite and radium-free tailings production are expected with obvious environmental advantages.

Iron was found to be extracted (i.e., reported in solution) at a lesser degree than sulphur apparently due to the hydrolysis problem discussed in the Theoretical Considerations section. Iron hydrolysis products were easily detected for those tests conducted at or higher than 150°C from the reddish colour of residues.

Thorium and Rare Earths

Extraction levels in the range of 50 to 60% were obtained for thorium from the various tests conducted as can be seen in Table 6. This level of thorium extraction is comparable to that also obtained with today's conventional atmospheric leaching practice at Elliot Lake (7).

Rare earths extraction was much more difficult with the best results (15-20%) obtained at the high temperature and solids concentration conditions (175°, 60% solids) where high sulphuric acid production was also obtained. At low temperatures and pulp densities almost no extraction of rare earths was

observed. These results are well explained on the basis of the well known refractory nature of monazite (carrier of RE's and Th) which breaks down only under high temperature and consentrated sulphuric acid conditions (46). Also, analysis of a number of final residues for SiO_2, Al, K and TiO_2, showed no measurable extraction had taken place except for TiO_2 (~50% extraction). Thus it might be expected that solvent extraction processing of the pressure leach solutions would offer some advantages in comparison with conventional leach solutions (i.e., no crud formation in SX circuits) (47).

PART II - PRESSURE LEACHING IN PRESENCE OF SALT CHLORIDES

In this series of experiments enhancement of radium extraction was investigated by adding various chloride salts in the pressure slurry. From the results presented in Part I it appears that pressure leaching at either 125°C/345 kPa or 150°C/103 kPa with 60% solids would give a reasonable compromise of relatively higher uranium extraction and increased radium mobility. Adoption of the first pair of conditions was made as having less tendency in producing excess sulphate concentration. Also it was decided that a 50% solids concentration be adopted as a basis for this group of experiments.

Evaluation of Various Chemical Additions

It has been demonstrated with various studies reported in the literature (2) that chloride salts such as NaCl, KCl, $CaCl_2$ hydrochloric acid, and EDTA promote radium release from uranium mill tailings. Thus pressure leaching tests were conducted at 125°C, 345 kPa O_2 and 50% solids in presence of 1.0 M salt chloride, 0.37, HCl and 0.1 M Na_2 EDTA to study the effect these additions have on radium extraction. The results obtained are summarized in Table 7. Best results were obtained with $CaCl_2$ while HCl and Na_2 EDTA gave a poor performance.

The improved radium extraction with $CaCl_2$ addition is attributed to removal of sulphate ions from solution in the form of gypsum precipitation. Efective removal of sulphate sulphur as calcium sulphate with calcium chloride additions have been reported in the literature for other leaching systems (47,48). Evidently, no significant coprecipitation of radium takes place in the present system since $CaSO_4$ is not as efficient a carrier for radium as $BaSO_4$ (42b). Also due to the considerable different sizes of the corresponding ionic radii [1.37°A(Ra) vs 0.99°A(Ca)] (42C) and the relatively short con-

tact time no significant exchange between radium in solution and calcium in the precipitate is believed to take place. Increased calcium and sulphate sulhur contents found in the residue further support $CaSO_4$ precipitation. On the other hand, jarosite is believed to form when KCl is used since an increased amount of potassium was found in residue in this case.

All the above tests with the exception of that of HCl addition gave low uranium extractions (88 to 90%) due to the associated neutralizing effect with salt additions. The test with HCl gave over 95% uranium extraction, thus it was decided in a subsequent series of tests that mixtures of $CaCl_2$ and HCl would be used.

Effect of $CaCl_2$/HCl Mixtures

Extraction curves for uranium and radium using 1.0 M $CaCl_2$ solutions acidified with various amounts of HCl are shown in Fig. 7. The uranium picture is clear; increased uranium extractions were obtained with increased acid additions. Radium extractions also increased initially with increasing acid concentrations but this beneficial effect was almost cancelled out with longer leach times (6 h). Best results (95% U and 69% Ra) were obtained at 4 h with 1.0 M $CaCL_2$/0.44M HCl. The initial beneficial effect of HCl addition on radium extraction might be in part due to lower pH which supresses radium absorption (42c).

Significantly more iron was found to report in solution in the chloride system than in the case of the sulphate system but Fe^{3+}/Fe^{2+} ratios did not alter. However, measured redox potential was found to be higher in the chloride system in agreement with published data (49). Elemental sulphur was found to form at comparable quantities in both systems.

The results from some additional tests conducted at different conditions are shown in Table 8. Comparison of runs No. 18 and 14 reveals that using a relatively low pulp density (25% solids) results in significantly improved radium extraction (90%). Also, comparison of runs No. 17 and 24 as well as No. 18 and 25 show that lower $CaCl_2$ concentration results in lower radium extraction. Thus the results of these tests indicate that a high ratio of $CaCl_2$ concentration to solids concentration is required for achieving high radium extractions. This might be explained in terms of the supressing effect strong salt clorides have on the activity of sulphate ion (50) and the resulting higher solubility for $RaSO_4$ [or equivalently $BaSO_4$ (43)]. The effective-

ness of $CaCl_2$/HCl mixtures in enhancing radium extraction during pressure leaching of uranium ores is further illustrated with runs No. 19 and 19A of Table 8.

During the course of this experimental work slow precipitation of gypsum was observed from the leach solution samples long after (> 1 day) filtration and washing of residues had been employed. X-ray diffraction analysis identified two precipitate structures, $CaSO_4.2H_2O_1$ (gypsum) and $CaSO_4$ .1/2 H_2O (plaster of Paris). Radiological analysis of these precipitates showed a high radium concentration (~30,000 pCi/g). In other words under the applied leaching conditions the apparent solubility of $CaSO_4$ is significant; i.e., the leach solutions are supersaturated in $CaSO_4$ and this is the reason for the subsequent precipitation described. Similar behaviour for gypsum has also been observed in zinc hydrometallurgical solutions (51). This macroscopic observation of supersaturation in the case of $CaSO_4$ is an indirect confirmation of our suggestion that "increased" radium sulphate solubility in the complex pressure leach solution explains the relatively high radium mobility.

Acidification of the analytical samples with strong HCl appeared to prevent this precipitation of gypsum. Therefore, measures should be taken in a possible uranium leach circuit where radium is dissolved simultaneously with uranium for advance and effective removal of radium from solution to avoid contamination of subsequent steps in the process.

Second-Stage Leach

Best results from the one-stage leaches were obtained by using 25% solids slurries combining also at least 1.0 M $CaCl_2$/0.037 M HCl at 125°C and 345 kPa oxygen pressure. Thus uranium extraction was $\geq$95% while the final leach residues (6 h leach time) contained ~40 pCi/g Ra^{226} i.e., 90% radium extraction into solution was achieved. To lower even further the residual radium content of the uranium tailings as well as to allow higher pulp densities to be employed, a two stage leaching scheme was explored.

Samples of residues from pressure leaches at high pulp densities (50-60%) with or without the addition of $CaCl_2$/HCl mixtures were treated separately either by employing pressure leaching at 125°C with 103 kPa oxygen overpressure or by atmospheric leaching at 70°C. Both leaches were conducted with 0.1 M HCl in the presence of $CaCl_2$ at reduced pulp densities (25-33%

solids). Atmospheric leaching proved more efficient for radium removal apparently due to a lesser tendency for sulphate production than in the case of the pressure leach. The second stage atmospheric leaching results along with the leaching conditions employed and the composition of the first stage residues used are summarized in Table 9.

These results clearly suggest that significant radium removal should be achieved during the first stage pressure leach if very low residual radium concentrations are sought during the second stage atmospheric leach. Radium concentration in the first stage leach residue should be in the range of 100-120 pCi/g in order to obtain a final residue (i.e., after second stage leaching) containing Ra 40 pCi/g solids.

Since some of the uranium remains unleached in the final residues then some radium-226 will also be present assuming both are in secular equilibrium. Thus for a residual 0.006% U concentration (94.5% extraction) 20 pCi/g Ra^{226} is expected to be in equilibrium. Calculations made by Nirdosh et al. (37) have indicated that an hysteresis in radium extraction occurs resulting in 20 pCi/g deviation of the residual radium concentration from that expected from secular equilibrium considerations. Thus the somewhat higher than 20 pCi/g residual radium concentration found here is in agreement with previously reported calculations (37).

Although other radionuclides such as Pb^{210} were not considered in the present work, predictions based on previous reported results (48) suggest that at least Pb^{210} would be solubilized and extracted along with Ra^{226}.

Finally, it is of interest to note that in a possible process flowsheet $CaCl_2$ could be recycled for economic as well as ecological reasons (48). Further compensation of the anticipated increased operating cost of a plant based on the present process is expected on the grounds that long term monitoring and treatment ($BaCl_2$ precipitation method) of the uranium tailings and their effluents would be almost eliminated.

CONCLUSIONS

Although a number of investigations have been reported previously on acid pressure leaching of uranium ores, this is the first time that uranium and radium extraction have been considered simultaneously.

This work shows that appropriate selection of experimental conditions for pressure leaching of sulphidic type uranium ores allows enhanced radium extraction (~30%) and simultaneously high uranium recovery (94%). This can be achieved by operating at moderate temperatures (125 to 150°C) and with short leaching times (4 to 6 h) to avoid excessive sulphate production and subsequent precipitation of $RaSO_4$.

On the other hand, pressure leaching at temperatures as high as 175°C does not improve extraction of thorium (maximum attained 60%) and of rare earths (maximum attained 20%) over conventional atmospheric H_2SO_4 leaching. This low extraction is due to the refractory nature of the monazite present in the ore.

The addition of various salt chlorides in the pressure leach slurry substantially improves radium extraction levels. Mixtures of $CaCl_2$/HCl (1-2 M/0.037-0.1 M) are, however, the most effective means in achieving high radium extraction; this being due to sulphate removal from the leach solution by $CaSO_4$ precipitation. The $CaCl_2$ to solids ratio controls the final radium level in the pressure leach residue. Thus one stage pressure leaching at 125°C, and 345 kPa O_2 with 25% solids and 2 M $CaCl_2$/0.1 M HCl addition results in a very low residual radium concentration (36 pCi/g). Tailings can then be disposed with minimized environmental impact. The requirement for operating at lower pulp densities than conventionally, is not expected to affect the prouction capacity of a given plant employing the present process since much shorter retention times are used in this process.

Operation at conventional pulp densities (50-60% solids) during pressure leaching is also possible but in this case a second leach stage at 70°C under atmospheric pressure with $CaCl_2$/HCl as leaching medium should follow in order to render tailings almost free of radionuclides (~40 pCi/g Ra^{226}). This two-stage scheme would allow full utilization of the working capacity of the pressure reactors thus savings in capital expenditures may be anticipated.

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TABLE CAPTIONS

Table 1 Chemical analysis of Elliot Lake uranium ore

Table 2 Uranium, radium and sulphur extraction after 6 h under various pressure leaching conditions

Table 3 Effect of pulp density on solution chemistry and uranium and radium extraction levels (experimental conditions: 125°C, 345 kPa O_2, 6 h)

Table 4 Effect of $CuSO_4$ addition on Fe^{+++}/Fe^{++} ratio, and on uranium extraction

Table 5 Distribution of sulphur species under various pressure leaching conditions

Table 6 Per cent thorium extracted after 6 h under various pressure leaching conditions

Table 7 Effect of various chemical additions on radium extraction (experimental conditions: 125°C; 345 kPa O_2; 50% solids)

Table 8 Uranium and radium extraction data from a number of pressure leaching runs conducted under a combination of experimental conditions

Table 9 Second stage atmospheric leaching tests conducted using residues from first stage pressure leaches

FIGURE CAPTIONS

Fig. 1 Effect of temperature on uranium and radium extraction (experimental conditions: 103 kPa O_2; 60% solids)

Fig. 2 Effect of partial oxygen pressure on uranium and radium extraction (experimental conditions: 125°C; 60% solids)

Fig. 3 Effect of pulp density on uranium and radium extraction (experimental conditions: 125°C; 345 kPa O_2)

Fig. 4 Variation of sulphate production with time at various temperatures and partial oxygen pressures

Fig. 5 Variation of pH with time at various temperatures and partial oxygen pressures

Fig. 6 Variation of ferric to ferrous ratio and EMF with time at various temperatures and partial oxygen pressures. (Conditions and symbols same as in Fig. 5)

Fig. 7 Effect of $CaCl_2$/HCl mixtures on uranium and radium extraction. (Experimental conditions: 125°C; 345 kPa O_2; 50% solids)

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Table 1. Chemical Analysis of Elliot Lake Uranium Ore

CONSTITUENT	WEIGHT %	CONSTITUENT	WEIGHT %
U	0.11	SiO_2	83.34
Ra	381 pCi/g	Al	3.47
Th	0.037	Mg	0.14
RE's (total)	0.15	Ca	0.19
Fe	3.37	K	1.88
S (total)	3.05	TiO_2	0.46
S (SO_4)	0.26	P	0.024
S^o	0.01	C (total)	0.07

Table 2. Uranium, Radium and Sulphur Extraction After 6 Hours Under Pressure Leaching Conditions

LEACHING CONDITIONS			PERCENT EXTRACTION AFTER 6 HOURS		
Temp ^{o}C	PO_2 KPa	Pulp Density % solids	URANIUM	RADIUM	SULPHUR
125	103	60	91.6	28.0	20.5
125	345	60	94.5	26.5	31.6
125	517	60	93.6	21.0	27.5
150	103	60	94.4	35.0	33.2
150	345	60	94.0	16.5	50.1
175	103	60	94.7	9.0	59.6
125	345	50	93.1	34.5	22.4
125	345	40	92.9	34.5	25.3

Table 3. Effect of Pulp Density on Solution Chemistry And Uranium and Radium Extraction Levels (Experimental Conditions: 125°C; 345 KPa O_2, 6 h)

PULP DENSITY % SOLIDS	SOLUTION				EXTRACTION (%)	
	pH	$SO_4^=$ (g/L)	Fe^{+++} (g/L)	Fe^{+++}/Fe^{++}	U	Ra
60	1.10	43.4	1.91	0.59	94.5	26.5
50	1.18	20.5	0.42	0.27	93.1	34.5
40	1.54	15.4	0.3	0.26	92.9	34.5

Table 4. Effect of $CuSO_4$ Addition on Fe^{+++}/Fe^{++} Ratio and Uranium Extraction

LEACHING CONDITIONS 125°C; 345 KPa O_2; 50% solids	SOLUTION				URANIUM EXTRACTION	
	pH		Fe^{+++}/Fe^{++}		(%)	
LEACH TIME (Hours)	-	$CuSO_4$ 0.1 M	-	$CuSO_4$ 0.1 M	-	$CuSO_4$ 0.1 M
1	1.92	2.20	0.04	0.15	87.5	89.2
2	1.60	1.89	0.05	0.45	89.3	90.2
4	1.35	1.78	0.27	0.58	91.5	91.6
6	1.18	1.25	0.27	0.98	93.1	93.0

Table 5. Distribution of Sulphur Species Under Various Pressure Leaching Conditions

LEACHING CONDITIONS				DISTRIBUTION OF SULPHUR SPECIES			
				RESIDUE			SOLUTION
LEACH TIME 6 Hours	Temp °C	PO_2 KPa	Pulp Density % sol.	S^{2-} %	$S(SO_4)$ %	S^o %	$S(SO_4)$ %
	FEED			91.8	7.9	0.3	-
	125	345	60	56.3	8.9	3.2	31.6
	125	345	50	52.8	6.4	18.4	22.4
	125	517	60	55.0	7.6	9.9	27.5
	150	345	60	32.5	14.6	2.8	50.1
	175	345	40	16.8	11.1	1.0	71.1

Table 6. Percent Thorium Extracted After 6 Hours Under Various Pressure Leaching Conditions

LEACHING CONDITIONS			THORIUM EXTRACTION (%)
Temp ^{o}C	PO_2 KPa	% solids	
125	103	60	50
125	345	60	55
125	517	60	60
150	103	60	58
150	345	60	53
175	103	60	58
125	345	50	47
125	345	40	52
125	345	50	52

Table 7. Effect of Various Chemical Additions on Radium Extraction (Experimental Conditions: 125°C; 345 KPa O_2; 50% solids)

LEACH TIME (Hours)	PER CENT RADIUM EXTRACTION					
	HCl 0.37 M	NaCl 1.0 M	KCl[1] 1.0 M	$CaCl_2$ 1.0 M	Na_2 EDTA 0.1 M	No Addition
2	4.5	9.7	16.0	43.8	0.0	14.0
4	7.4	11.5	12.0	50.1	6.4	27.3
6	1.5	19.8	28.0	53.3	7.0	34.5

1. Acidified with 0.037 M HCl.

Table 8. Uranium and Radium Extraction Data from a Number of Pressure Leaching Runs Conducted Under a Combination of Experimental Conditions

Run No.	LEACHING CONDITIONS					PER CENT EXTRACTION					
	Temp °C	PO_2 KPa	Pulp Density % Solids	$CaCl_2$ M	HCl M	2 h Leach		4 h Leach		6 h Leach	
						U	Ra	U	Ra	U	Ra
18	125	345	25	1.0	0.037	N/A	N/A	94.0	86.4	94.9	89.3
14	125	345	50	1.0	0.037	86.6	47.7	91.1	53.2	93.1	54.5
17	125	345	50	1.0	0.1	90.2	60.4	92.2	54.0	94.2	53.5
24	125	345	50	0.5	0.1	N/A	N/A	91.1	25.0	92.1	24.0
25	125	345	25	2.0	0.1	N/A	N/A	95.1	89.0	96.1	91.0
19	125	103	60	1.0	0.037	88.4	48.5	91.1	55.3	92.2	57.6
19 A	150	103	60	1.0	0.037	87.5	51.9	89.4	64.3	92.9	72.0

Table 9. Second Stage Atmospheric Leaching Tests Conducted Using Residues from First Stage Pressure Leaches

SECOND STAGE LEACH — ATMOSPHERIC					OVERALL EXTRACTION (Both Stages)	
FEED[1]		LEACHING CONDITIONS	RESIDUE			
U %	Ra pCi/g		U %	Ra pCi/g	U %	Ra %
0.012	334	70°C; 25% solids; 6 h 1.0 M $CaCl_2$/0.1 M HCl	0.008	109	93.0	72
0.009	298	70°C; 25% solids, 6 h 1.0 M $CaCl_2$/0.1 M HCl	0.006	98	94.5	75
0.006	112	70°C; 25% solids; 6 h 2.0 M $CaCl_2$/0.1 M HCl	0.006	41	94.5	89.5

1 Residues from First Stage Pressure Leach

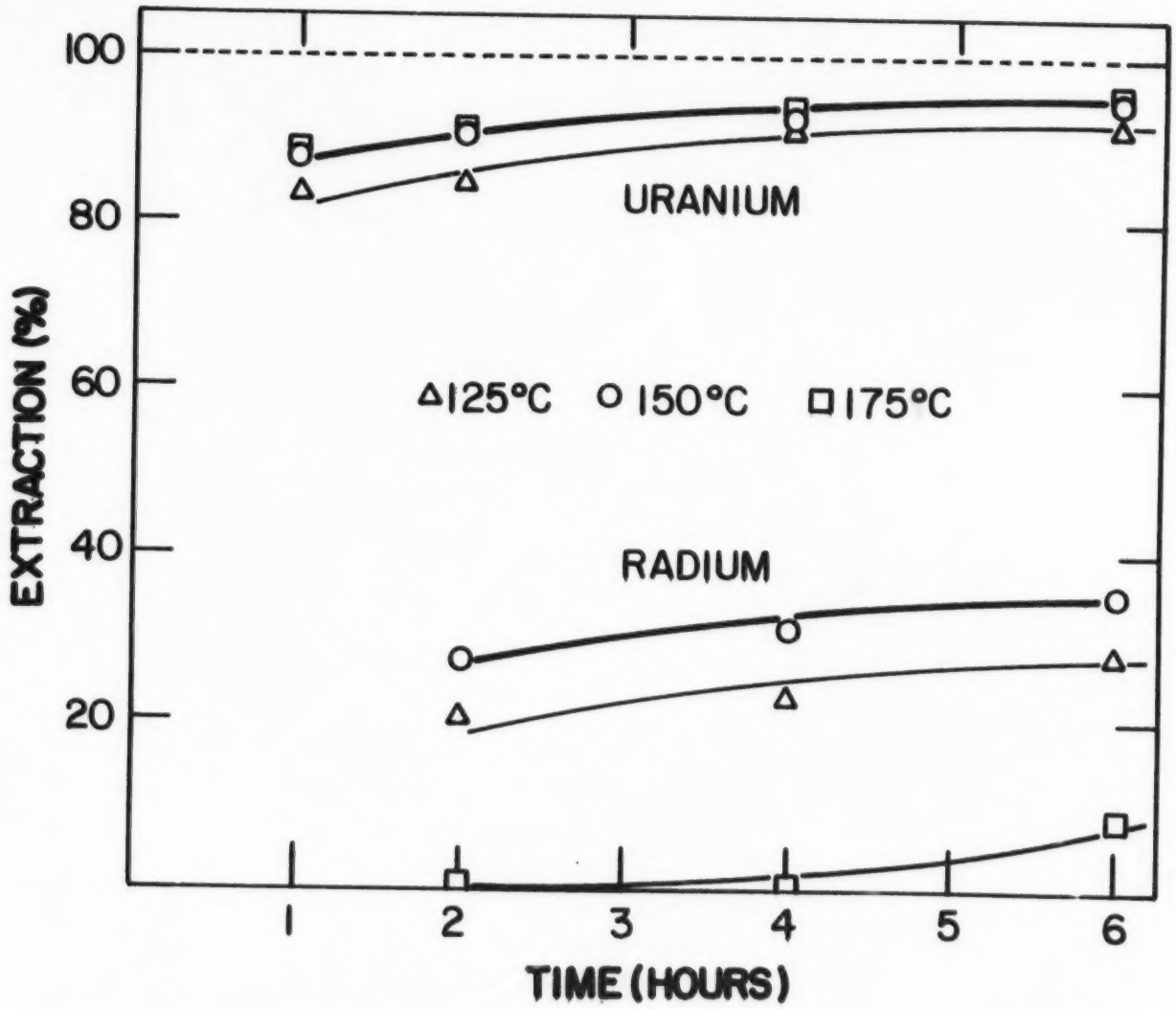

Fig. 1 Effect of temperature on uranium and radium extraction (experimental conditions: 103 kPa O_2; 60% solids).

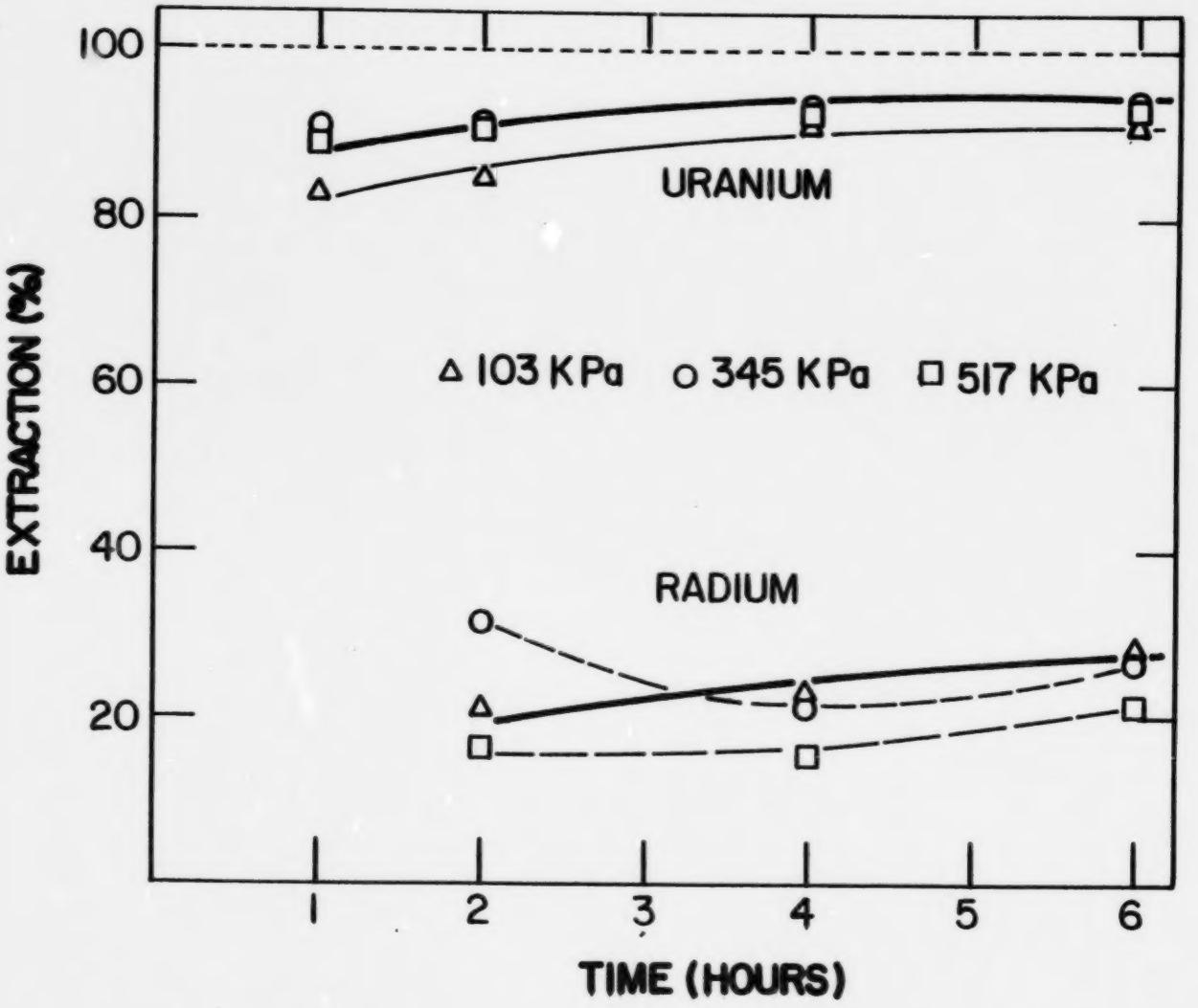

Fig. 2 Effect of partial oxygen pressure on uranium and radium extraction (experimental conditions: 125°C; 60% solids).

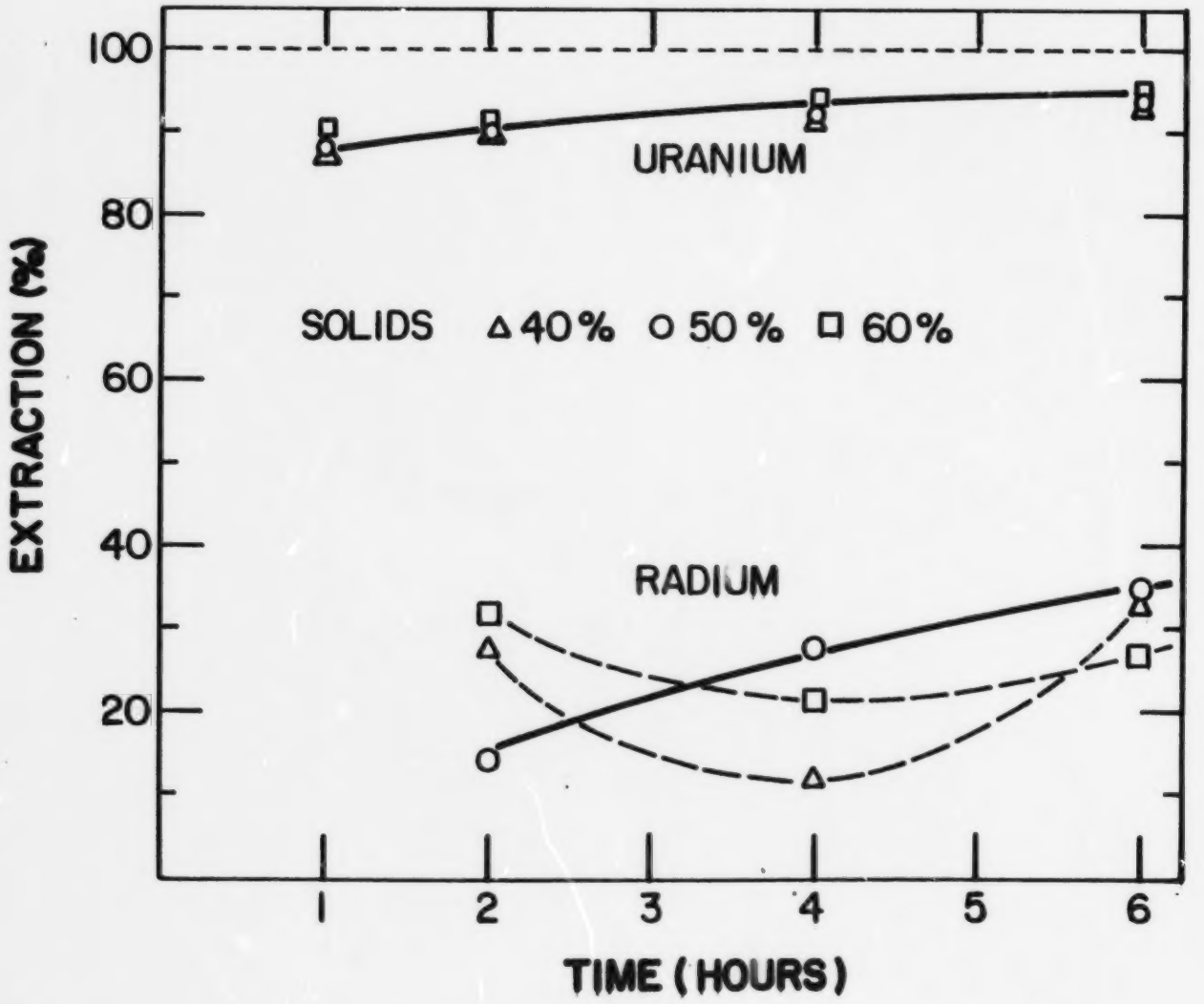

Fig. 3 Effect of pulp density on uranium and radium extraction (experimental conditions: 125°C; 345 kPa O_2).

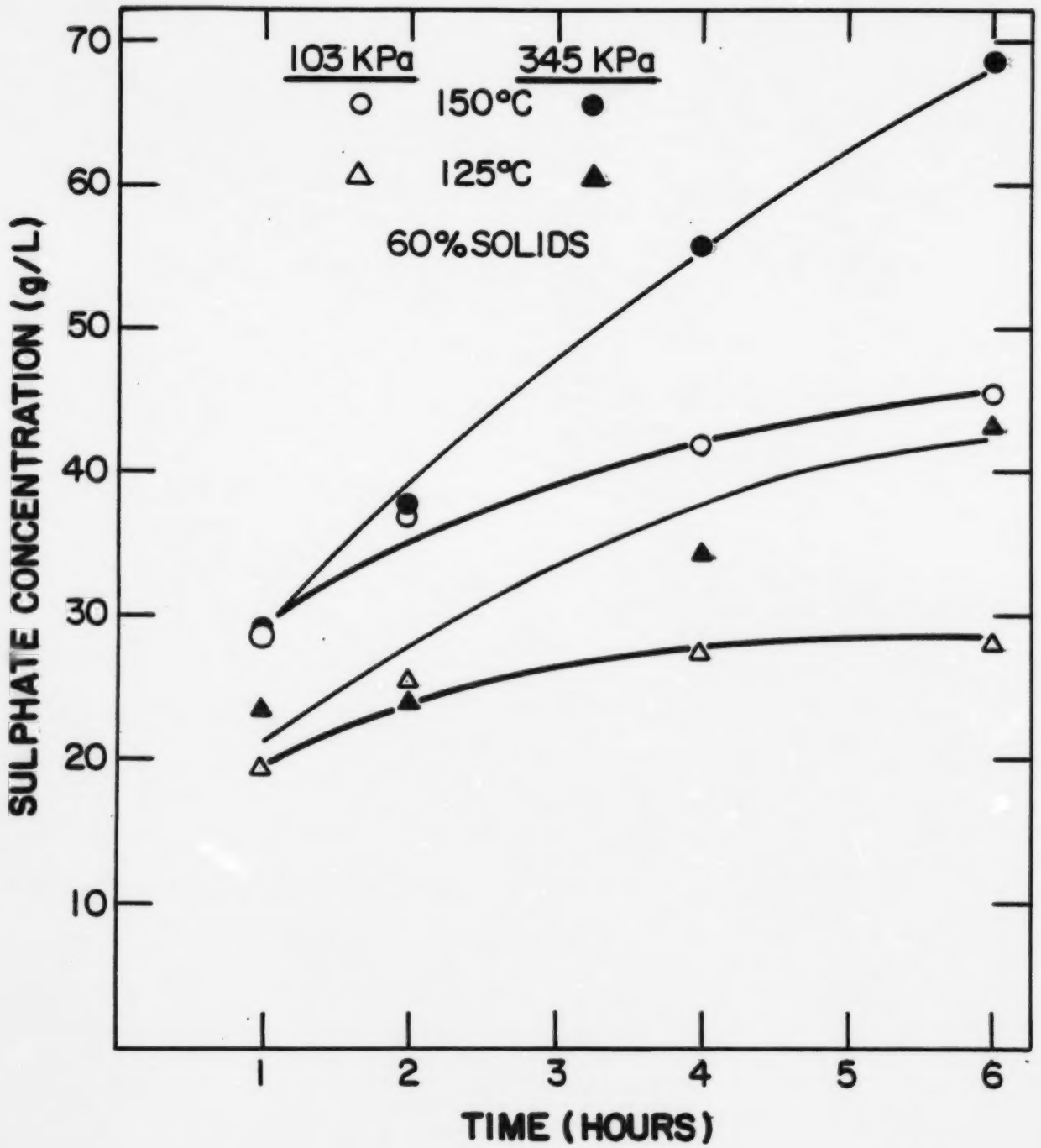

Fig. 4 Variation of sulphate production with time at various temperatures and partial oxygen pressures.

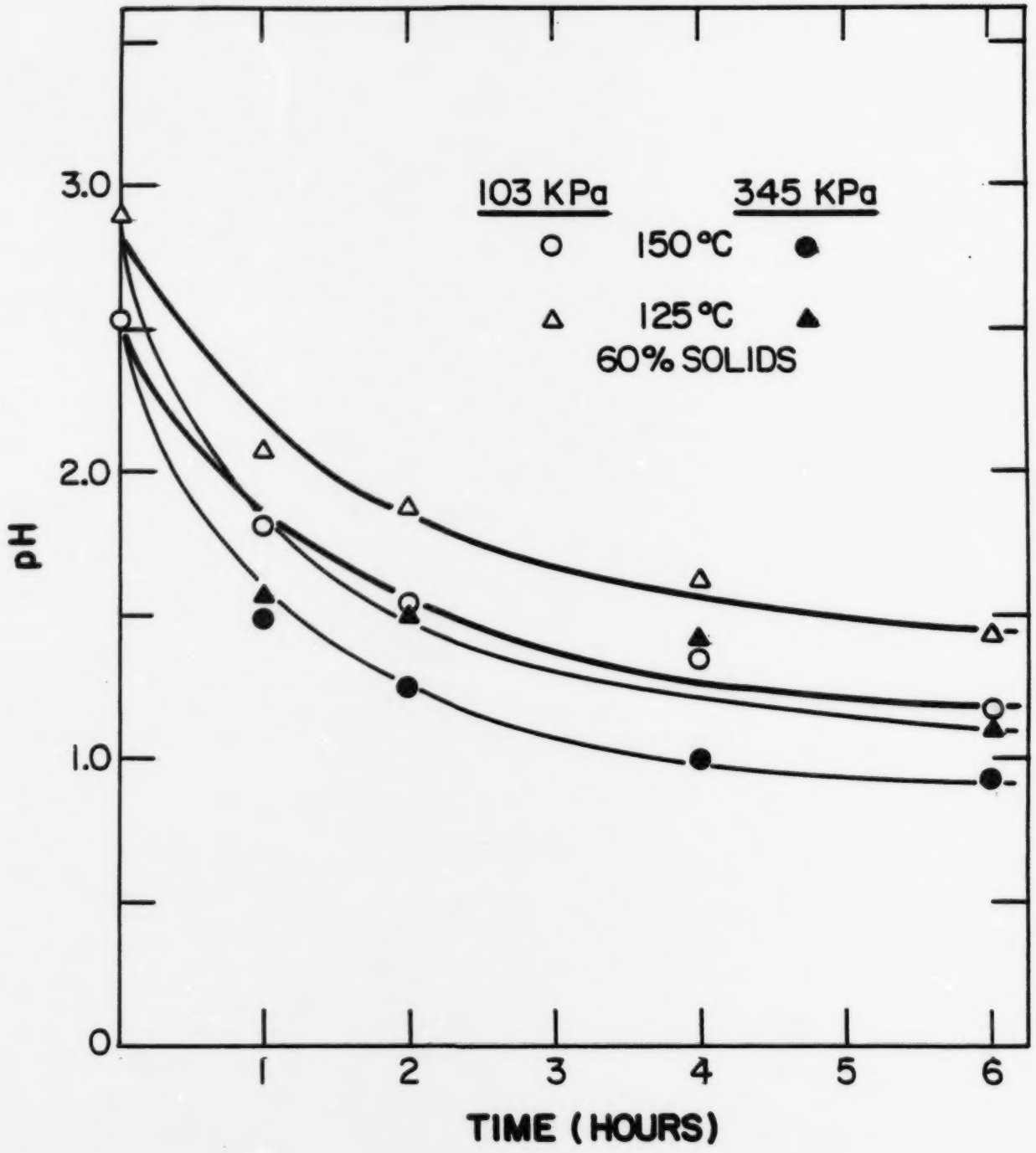

Fig. 5 Variation of pH with time at various temperatures and partial oxygen pressures.

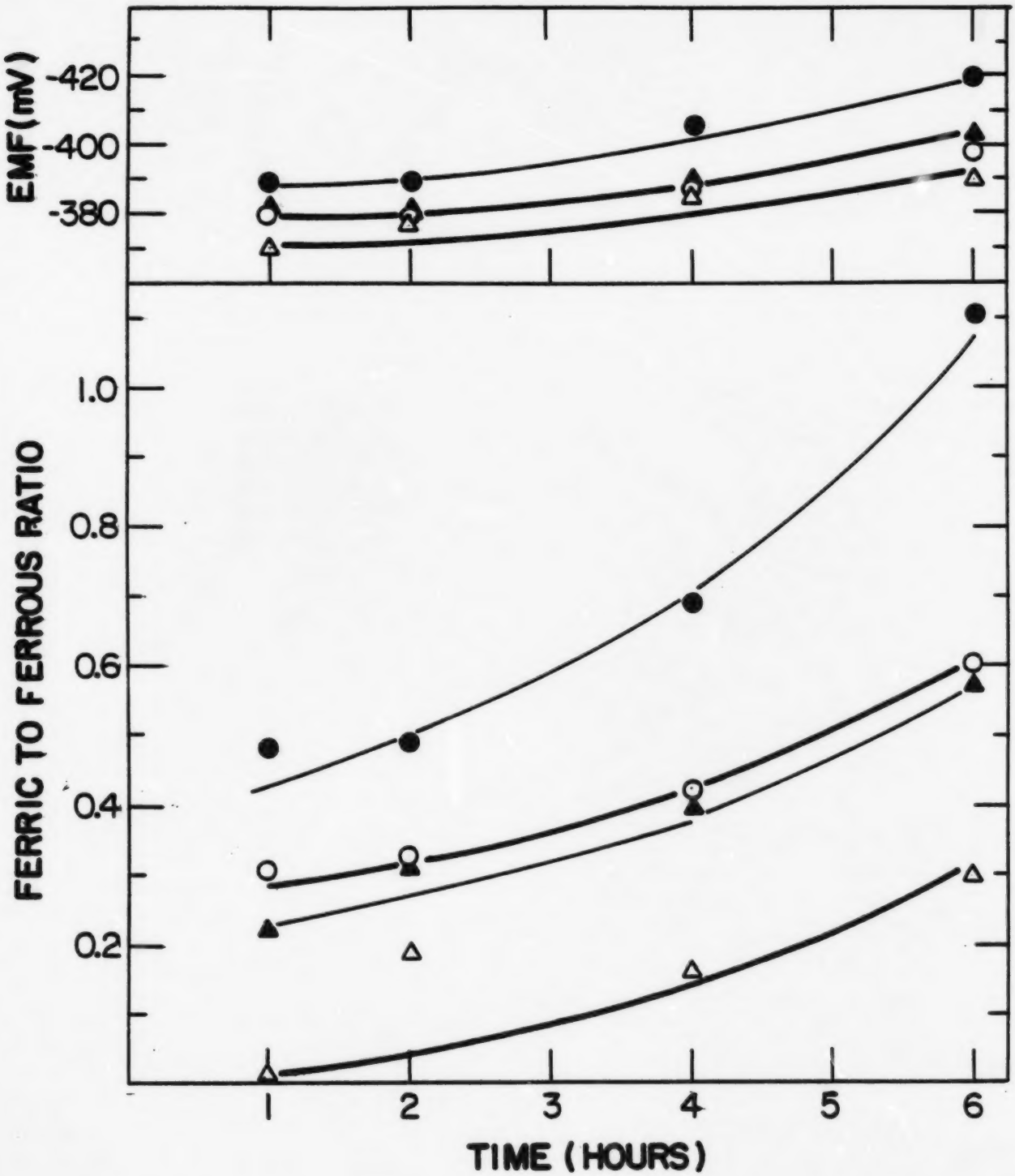

Fig. 6 Variation of ferric to ferrous ratio and EMF with time at various temperatures and partial oxygen pressures. (Conditions and symbols same as in Fig. 5)

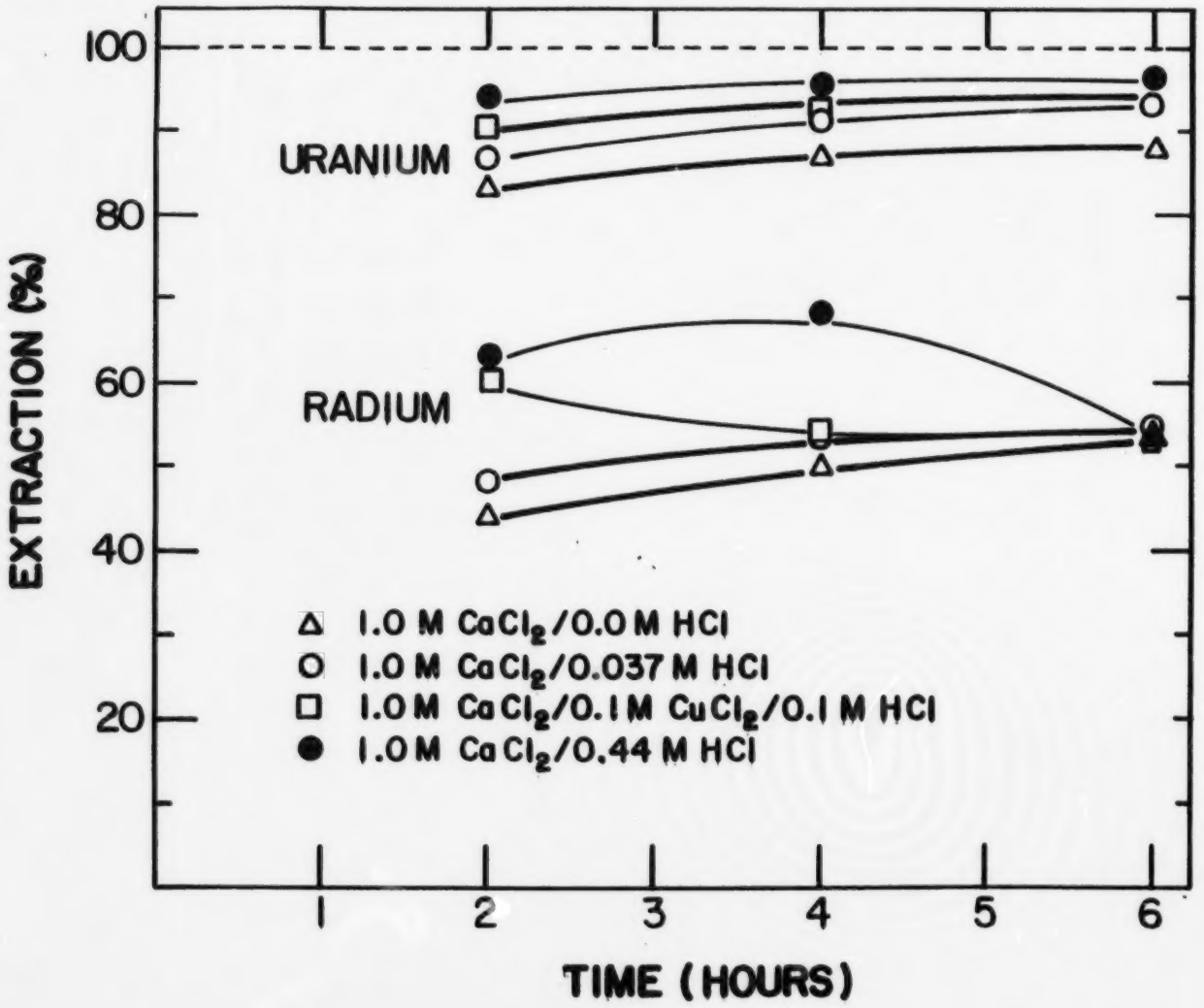

Fig. 7 Effect of $CaCl_2$/HCl mixtures on uranium and radium extraction. (Experimental conditions: 125°C; 345 kPa O_2; 50% solids).